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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

ON EVAPORATION FROM THE SURFACE OF A SOLID SPHERE.

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PRELIMINARY NOTE.

By Harry W. Morse.

Presented by John Trowbridge, February 9, 1910. Received January 3, 1910.

The micro-balance of Salvioni and Nernst permits of following small changes in weight with considerable accuracy, provided the body under investigation has a mass not greater than a few milligrams. This balance consists merely of a fibre of quartz or glass, firmly held in a nearly horizontal position by being secured at one end, and provided at the other end with some means of attaching the object to be weighed. The weight is then, within quite wide limits of deflection, proportional to the deflection, and the balance is easily calibrated by means of small riders of known weight. Deflections are followed by means of a cathetometer or a microscope with micrometer eyepiece. Differences of 0.01 millimeter or even less are easily determined, and if the fibre be so chosen that a weight of 1 milligram gives a deflection of about a centimeter, there is no difficulty in detecting and measuring changes of weight of 0.001 milligram or less.

With such a balance the change of weight of small spheres of iodine has been followed at approximately constant temperature. Evaporation was allowed to go on in a large box with glass sides, and the two side doors of the case were left open before each series of readings to allow free circulation of air. It may therefore be assumed that the partial vapor pressure of iodine in the atmosphere about the evaporating spheres was constant. The temperature was constant within about 0.3° during each run.

After many attempts to obtain definite geometrical form by casting, fairly accurate spheres were made by pouring molten iodine into water. There is no difficulty in obtaining in this way approximately spherical pieces with radii varying from 1 millimeter down to 0.2 millimeter.

It was thought possible that there might be a change in the character of the surface as evaporation proceeded. The spheres were hard on the surface, and quite smooth as they came from the water, but they undoubtedly consist of a mass of very small irregular crystals and any roughening that might appear during the course of the experiment would lead to a considerable increase in surface. That such changes do not occur in disturbing amount is shown by the fact that the determinations made with small spheres fresh from formation fall accurately on the curve of measurements on spheres which have been evaporating for some hours. Microscopic examination corroborates this and shows also that the spherical shape is maintained practically unchanged until the sphere finally disappears completely.

In these experiments the spheres were supported on a nearly flat scale-pan of thin glass. This may introduce a variation in the surface exposed to the air, due to difference in the surface of contact between sphere and glass, and especially to be expected if the particles are not closely spherical. This factor is also shown to be negligible by the closeness with which the spherical form is kept during evaporation and also by the fact that turning the particle over has no measurable effect on the rate of evaporation.

Measurements on three spheres of different radii are given below.

These observations are plotted in the curve of Figure 1.

There is plenty of evidence that in any system made up of smaller and larger particles of the same substance, whether solid or liquid, the smaller particles are relatively unstable. So far, however, all of our knowledge about solids is of a purely qualitative nature, and no definite relation has ever been obtained based on vapor pressure or surface tension, and expressing quantitatively the change of vapor pressure or surface tension with change of radius. It has been many times noticed that, in a sealed tube containing iodine crystals of various sizes, the larger crystals grow at the expense of the smaller ones, which gradually disappear. In a few days this can be clearly proved, and the same effect has been noticed for water drops and for camphor and other rather volatile substances.

In the case of liquids it is possible to set up a definite relation between vapor pressure and curvature of drop. This has been done for water and a few other liquids, and the theory has been tested with some accuracy by experiments on the formation of fog by the expansion of saturated water vapor. For water the difference in vapor pressure between a drop of radius 0.001 millimeter and a flat surface is of the order of 0.001 mm. of mercury, so that the effect becomes almost insensible for drops of any size.

It was therefore expected that any influence of the size of the particle of iodine on the rate of evaporation would only appear for very small

Sphere 1.		Sphere 2.		Sphere 3.	
Time.	Weight.	Time.	Weight.	Time.	Weight.
min.	mgms.	min.	mgms.	min.	mgms.
0	1.880				
20	1.770				
63	1.600				
103	1.420				
131	1.310				
140	1.260				
150	1.210				
169	1.140				
178	1.100				
189	1.050	187	1.066		
198	1.000	214	0.955		
295	0.638	228	0.907		
308	0.590	247	0.845		
319	0.557	263	0.759		
335	0.512	283	0.684	287	0.668
358	0.482	300	0.617	297	0.635
381	0.376	318	0.558	307	0.603
438	0.233	328	0.522	319	0.558
456	0.192	338	0.491	330	0.525
468	0.157	355	0.438	340	0.503
484	0.135	375	0.373		
498	0.104	390	0.337		
		456	0.160		
		466	0.147		
		476	0.126		
		486	0.105		
		496	0.087		
		506	0.070		
		521	0.048		
		531	0.036		
		536	0.028		
		542	0.022		
		548	0.017		
		554	0.011		
		560	0.006		
		576	0.000		

spheres indeed and that for all particles of sensible dimensions the rate would be proportional to the surface, so that

$$-\frac{dm}{dt} = ks;$$

or since the change in mass is being followed

$$-\frac{dm}{dt} = k_1 m^{\frac{2}{3}}.$$

The measurements show that this relation does not hold, even for spheres of radius 0.5 millimeter or more. The observed values do,

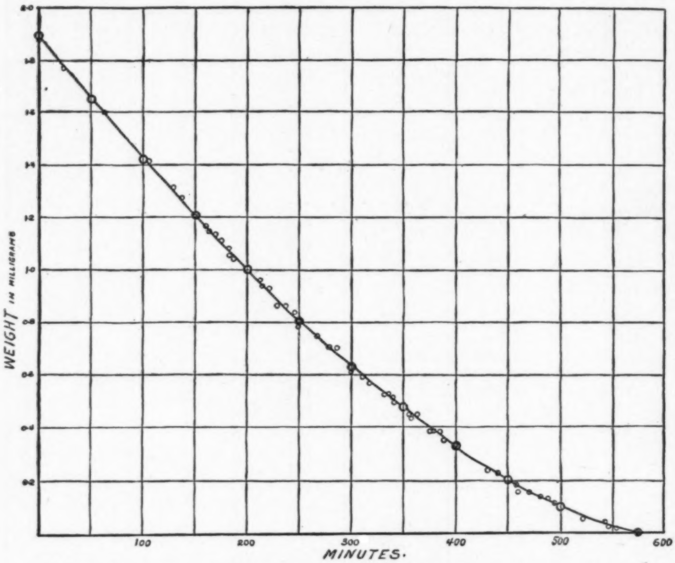

FIGURE 1. Evaporation from small spheres of Iodine. Small circles, observed values. Large circles, calculated values.

however, agree accurately with the assumption that the rate of evaporation is proportional to the surface and at the same time inversely as the radius, so that

$$-\frac{dm}{dt} = k\,\frac{s}{r} \quad \text{or} \quad -\frac{dm}{dt} = k_2 m^{\frac{1}{3}}.$$

In the figure the large circles have been placed according to the formula

$$\frac{m_1^{\frac{2}{3}} - m_2^{\frac{2}{3}}}{t_2 - t_1} = K,$$

and the curve has been drawn through the points thus determined. The constant was calculated from the mean of all the observations and shows a probable error of a little less than 0.5 per cent. The results of the observations are given as smaller circles. In putting in the results for the smaller spheres or for those in which a full run down to zero of weight was not carried out, the original value of the mass of the sphere was placed on the curve and the times of the other observations on the same sphere were taken from this point. It is very probable that this method of choosing the highest weight has somewhat decreased the accuracy of the calculated constant, for it has been invariably observed that a measurable time elapses before a sphere falls into its regular rate of evaporation. It begins slowly, sometimes at not more than half its full rate, and several minutes elapse before it reaches its maximum value. It is probable that better agreement would have been obtained if a point farther along in the observations had been chosen and calculations made in both directions from this.

It seems clear that for spheres of iodine of mass ranging from 2 milligrams to very small values, the rate of evaporation is quite accurately proportional to the *radius.*

Before taking up any theory of this surprising result it will be best to have data on evaporation from masses having other geometrical shapes, and especially for a flat surface. It is expected that data on these points will be presented to the Academy in the near future.

Jefferson Physical Laboratory,
Cambridge, Mass.,
December, 1909.